THE PREPARATION AND POLYMERIZATION OF SOME SUBSTITUTED BUTADIENES

BY

ROBERT LEE MYERS

B. S., Kent State University, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
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Introduction

GR-S is the emulsion copolymer of butadiene and styrene that was produced in large volume when the exigencies of World War II required a replacement for the supply of natural rubber that was no longer available. Certain inherent faults in this elastomer have been observed during use. These faults have been related[1] to the structural features of GR-S which are characterized by an over-all heterogeniety. One of the chief heterogeniety factors is that the butadiene can polymerize in a 1,2 manner as well as 1,4. Kolthoff[2] observed that isoprene, when copolymerized with styrene, gave more 1,4 addition of the diene units than did butadiene itself. This fact suggested that it would be desirable to study the effect of more bulky 2-alkyl groups on the amount of 1,4 addition. The purpose of this work was to devise a convenient synthesis of 2-alkylbutadienes. A second objective was to study the effect of substituting a monomer for styrene that would be more compatible with the butadiene chains.

Discussion of Results

A method of synthesis of 2-alkylbutadienes has been developed that appears to be general, limited only by the availability of the corresponding 2-alkylacetaldehydes. The method consists of three steps. In the first step, a Mannich reaction[3] is employed, using the alkylacetaldehyde, formaldehyde, and dimethylamine hydrochloride. The Mannich base hydrochloride is not isolated, but is decomposed by steam distillation to yield the α-alkylacrolein. This method of producing α-substituted acroleins appears to represent a general method that has not been widely developed. In the next step, the methyl Grignard reagent is added to the α-alkylacrolein to give on hydrolysis the 2-alkyl-3-hydroxy-

butene-1. In the final step, the 2-alkyl-3-hydroxybutene-1 is converted to the desired diene by dehydration over activated alumina. By this method 2-ethylbutadiene-1,3, 2-isopropylbutadiene-1,3, and 2-*n*-amylbutadiene-1,3 have been prepared starting respectively with *n*-butyraldehyde, isovaleraldehyde, and *n*-heptaldehyde.

In the dehydration of the 2-alkyl-3-hydroxybutene-1 derivtives, an interesting side reaction was observed that may be of preparatory value. In each case, in addition to the desired diene, there was isolated a ketone. In the case of the 2-ethyl-3-hydroxybutene-1, this ketone was identified as methyl *sec*-butyl ketone. This rearrangement may be best interpreted as arising from the addition of a mole of water to the original unsaturated carbinol to form a pinacol type intermediate, which could, under the influence of the acidic dehydration media, undergo a pinacol-pinacolone type rearrangement.

The preparation of 1-cyano-1,3-butadiene was also investigated. This diene was produced by the pyrolysis of the benzoyl ester of crotonaldehyde cyanohydrin.[4] The benzoyl ester of crotonaldehyde cyanohydrin was prepared[5] in one step by adding an aqueous sodium cyanide solution to a mixture of the acid chloride and crotonaldehyde at temperatures slightly below zero.

1-Cyano-1,3-butadiene was separated for the first time into its *cis* and *trans* isomers by fractional distillation. The configurations were assigned on the basis of the participation of only one isomer in Diels-Alder[6] reactions with butadiene and with maleic anhydride. This isomer was assigned the *trans* configuration and the isomer which did not participate, the *cis*. The *cis* isomer would not be expected to participate in Diels-Alder type reactions due to the steric inhibition of cyclization in the direction of ring closure imposed by the nitrile group. This steric inhibition has been observed[7] in the case of *cis*-piperylene which does not give an adduct with maleic anhydride, while the *trans* isomer does. 1-Cyano-

1,3-butadiene polymerized readily in bulk and in emulsion. It was copolymerized with butadiene, with styrene, and with methyl acrylate. The *trans* isomer polymerized faster with butadiene than did the *cis* isomer. The polymerization rates of the diene itself, and the copolymerization rates with butadiene appear to be of first order kinetics.

1-Cyano-2-methyl-1,3-butadiene was prepared in a manner exactly analogous to that employed for the 1-cyano-1,3-butadiene, using tiglic aldehyde(2-methylcrotonaldehyde) as the starting material. It was also polymerized in emulsion and copolymerized with butadiene in an emulsion system.

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VITA

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